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The Alpha-Brom Place Influence

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THE ALPHA-BROM PLACE INFLUENCE

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

George Edward Simpson

ENTITLED   The Alpha-Brom Place Influence

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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THE ALPHA-BROM PLACE INFLUENCE.

INTRODUCTION.

Is there not a better method for determining the structure of an organic compound than that now universally in vogue of analysing the substance for the elements, determining by certain class reactions the groups it contains, and fixing the position of these groups beyond doubt by comparison with a compound whose structure is already determined? This method is frequently very long, it is oftentimes uncertain, as the use of a certain reagent may cause a rearrangement, and it always so alters the original substance that it can be with difficulty replaced without practically starting from the ground up. Hence it is expensive, wasteful, and in the case of very small quantities of an unknown substance laboriously prepared, practically prohibitive. Chemists are at present earnestly endeavoring to find a new method of analysis. In their researches, some have discarded the older method almost entirely, the new being built on a new foundation, altho of course, any new method is possible only because of the many structuresproven by the old method. It is thought that inasmuch as physical characteristics are based on chemical composition and structure, a certain definite relation evidently exists between the two. The aim is to find the quantitative difference in a certain physical characteristic produced by the presence in a certain position of a certain group. If this can be accomp-

lished, the physical characteristics of an unknown, whichmay be easily and accurately measured, will predict the chemical structure. To illustrate by an example. It is seen that in general the addition of a methyl group to the aliphatic chain causes a rise in boiling-point. It is untenable that the influence of the methyl group varies spasmodically. For the physical character to be examined any one of a host may be chosen, melting-point, heat of combustion, crystalline structure, optical activity, electrical conductivity, etc.

The use of physical characteristics for the purpose of identification has several marked advantages: a large amount of the substance is not required. It is rapid and the substance can be recovered unchanged after examination, and for accurate results, purity of the substance is imperative. The electrical conductivity seems to offer a profitable characteristic for investigation, since certain organic substances ionize at least to a limited degree. In this paper the influence of bromine in the alpha position on the ionization of propionic acid is determined.

HISTORICAL.

The first chemist to recognize the fact that there exists a definite relation between ionization and structure was Ostwald (1) in 1889. He realized that the replacement of a hydrogen atom in an ionizable compound produced a change in the ionization of the substance. The influence of the halogen in a particular position he designated as the ratio

constant
of the ionization ∧of the substituted acid to that of the un-
substituted acid, and he named these factors according to
the position of the substituting group. thus:

$$\frac{K_\alpha}{K_o} = a, \qquad \frac{K_\beta}{K_o} = b, \qquad \frac{K_\gamma}{K_o} = c, \quad etc.$$

in which K_α, K_β, and K_γ are the ionization constants of the
alpha, beta, and gamma substituted acids, and K_o is the ioni-
zation constant of the unsubstituted acid. Thus the factor
a (influence) for bromine in the alpha position in propionic
acid would be $\frac{K_n}{K_o} = a$, in which constant K_n is the ionization
     alphabromo-
of ∧propionic acid, and a is the alpha factor for bromine in
alphabromopropionic acid. But in taking this ratio as the
measure of the influence of the substituted atom, Ostwald is
in error. This factor represents the ratio of the influence
upon ionization of all the atoms in the substituted acid to
those in the corresponding unsubstituted acid. It does not
represent the influence of the substituted atom alone upon
the ionization.

Theoretical.

Derick (2) has advanced the idea that the change in
the free energy of ionization of weak electrolytes is an
additive property. In other words, each atom in the mole-
cule exerts its influence upon the change in the free energy
of ionization independent of the other atoms in the electro-
lyte. In the working out of his quantitative measure of this
influence, the following formula is employed:

$$I = \frac{1}{A} = \frac{1}{RT \log K} = \frac{1}{aRT \log K},$$

in which A is the change in the free energy of ionization,

R is the gas constant,

T is the absolute temperature of measurement,

K is the ionization constant at $25°$,

a is the factor for converting natural logarithms to

the Brigg's or common logarithms, and

I is the summation of the influences of the atoms up-

on the change of the free energy of ionization.

But what is desired is not this summation of the influences of all the atoms in the molecule but rather the separate influence of a given substituent. In this work the influence of the alpha bromine atom in alphabromopropionic acid is desired. This influence $(I_{\alpha Br})$ is obtained from the expression :

$$I_{\alpha Br} = \frac{\text{Log } K_o}{\text{Log } K_n} - 1,$$

in which K_o is the ionization constant of propionic acid at $25°$, and K_n is the ionization constant of alphabromopropionic acid at $25°$. This expression is derived in the following manner: Since I_o and I_n are the influences of all the atoms in propionic and alphabromopropionic acids respectively upon the above function, then $I_o = b \dfrac{1}{\log K_o}$, and $I_n = b \dfrac{1}{\log K_n}$, from which $\dfrac{I_n}{I_o} = \dfrac{\log K_o}{\log K_n}$, since $b = \dfrac{1}{aRT}$ in each case. The other atoms $(CH_3 CH.COOH)$ in alphabromopropionic acid, excepting the bromine atom, differ from the atoms in propionic acid by a single hydrogen atom. Therefore,

$$I_{\alpha Br} - I_{\alpha H} = \frac{\log K_o}{\log K_n} - 1,$$

since in the above expression I_o is equal to one.
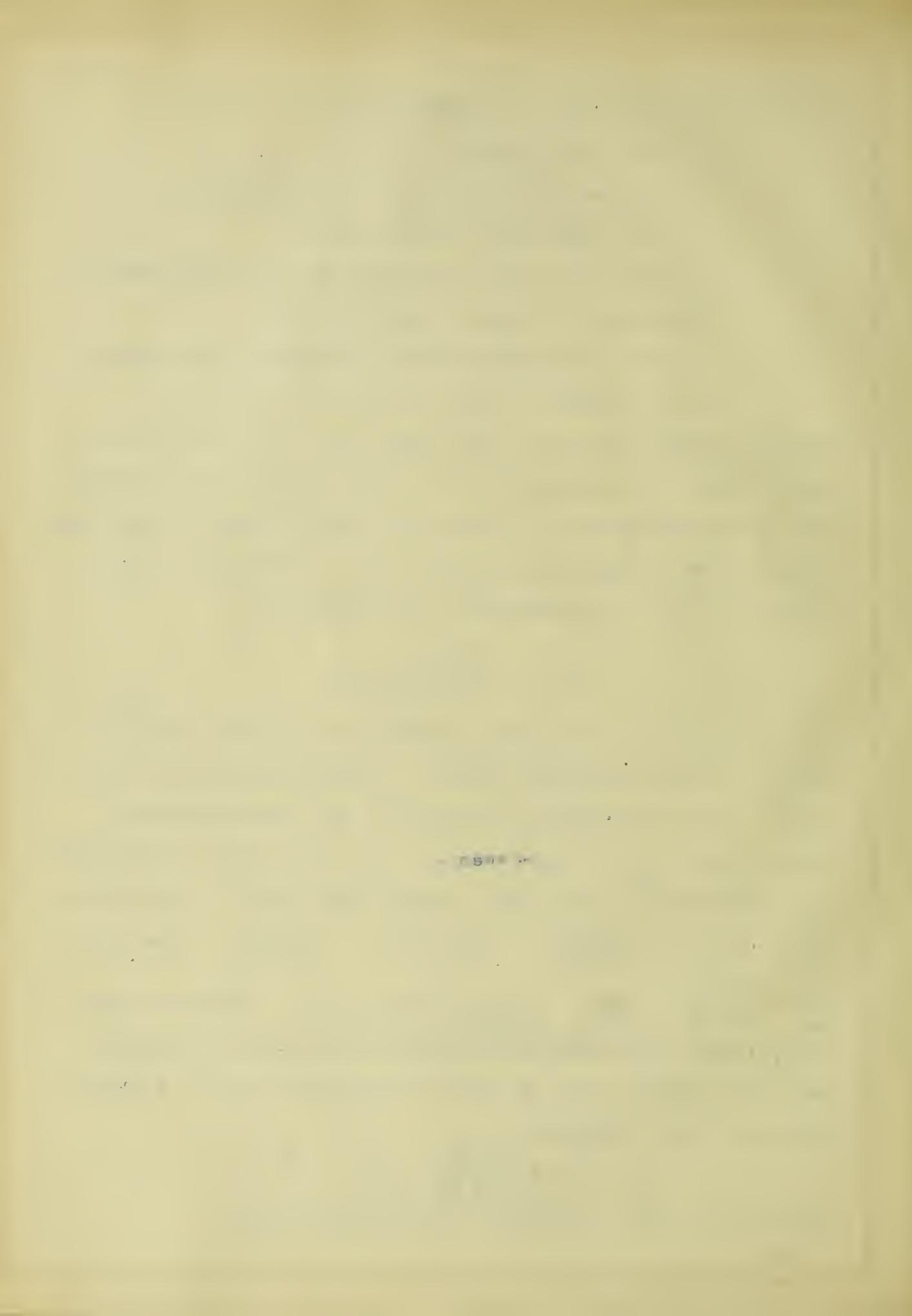
But the study of the unsaturated acids (3), together with the previous work of Derick, have shown that this $I_{\alpha H}$ is negligible compared with $I_{\alpha Br}$ when it occurs additively as above, hence;

$$I_{\alpha Br} = \frac{\log K_o}{\log K_n} - 1.$$

Derick, as a result of further investigations, found that for chlorine, bromine, hydroxyl, and some other groups, the relation existed as below, which relation he called the rule of thirds;

$$I_\alpha : I_\beta : I_\gamma, \text{ etc.} = I_\alpha ; \frac{I_\alpha}{3} ; \frac{I_\alpha}{9} , \text{ etc.}$$

Thus far, this rule has not been shown to apply to iodine with a reasonable degree of accuracy.

-: EXPERIMENTAL :-

Preparation of Alpha-Bromopropionic Acid.

A. Lactic Acid and Phosphorous Tribromide Method.

Thirteen grams of lactic acid was placed in a flask connected with a reflux condenser and placed on a steam bath. Ten grams of phosphorous tribromide was now cautiously added. There resulted a copious evolution of thick white fumes. After the reaction ceased, the resulting liquid was thrown into water to decompose the acyl bromide;

$$CH_3CH-Br-C\overset{O}{\underset{OBr}{}} \ + \ HOH = CH_3CH-Br-C\overset{O}{\underset{OH}{}} \ + \ HBr,$$
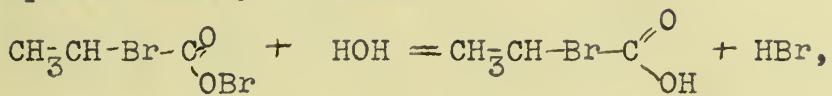
and then extracted with ether. The product from the ether extract gave a test for bromine, but as the quantity of the product was small, and as there was no more phosphorous tribromide on hand at the laboratory, another method for the preparation was sought.

B. Propionic Acid and Bromine Method.

Thirteen grams of bromine were now put in a sealed tube with twenty grams of propionic acid and heated in the bomb furnace for four hours at 125° to 130°. The bombs were then allowed to cool, after which they were opened and the hydrogen bromide driven out as far as possible by passing dry air thru the liquid. The mixture was then distilled under diminished pressure. That fraction boiling between 118° and 120° was analysed and found to contain sixty per cent of bromine, while the theoretical amount is 52.35 per cent. Accordingly, the fraction was redistilled until it came over at 118°. This fraction was being redistilled the last time, when the flask containing it broke under the pressure and the product was lost in the oil bath.

The same process was repeated and the following fractions secured:

Temp. bath	Inside Temp.	Pressure (mm)	Wt. Prod.
-115°	-103°	18	4.0 g.
110°-120°	107°-110°	18	21.o
115°-120°	112°-115°	18	10.5
128°-135°	117°-120°	18	23.0
130°-150°	120°-125°	17	13.o

The 117°-120° fraction was analysed and found to contain 60.01 per cent of bromine. The theoretical value for this acid is 66.03 per cent. The higher fraction, a mushy white mixture of solid and liquid was now examined. It was cooled and centrifuged to separate the solid from the liquid with which it was mixed, and the melting-point determined. This was not sharp, lying between 50° and 58° . The melting-point of this acid is given in Beilstein as 24.5^o , while that of the dibromo-acid is 61°. I therefore concluded that this product was a mixture of the two, and that the liquid which had been centrifuged out was probably the pure alpha-bromo product.

Conductivity of Alphabromopropionic Acid.
Apparatus: The flasks with which the conductivity water and acid came in contact, as well as all pipettes, stoppers (covered with tin foil), dropping funnels, etc., were thoroughly steamed for several days in order to remove any alkali that might be present. In making up the solutions, the acid was

weighed out on a balance calibrated to the fourth decimal place, and the solutions were made up by weight on a balance calibrated to the second place. The cell used for the water measurements was cylindrical in form and contained non-removable platinum electrodes. For the acid, a cell of the pipette form containing platinum-black electrodes was used. All conductivity measurements were taken on a calibrated slide-wire Wheatstone bridge; the resistance box was also calibrated. The cells were allowed to remain in the thermostat at 25° for several minutes before the measurements were taken.

Conductivity Water.

The water used in making the solutions was obtained by redistilling ordinary distilled water treated with alkaline permanganate. No water was collected until half the contents of the still (20 liters) had come over, and while collecting, half the distillate was allowed to escape as steam in order to preclude any danger of impurities from the air getting into the water. About five liters of water was collected and all measurements in which it was used were made within a day and a half after the water was obtained. From time to time the specific conductance of this water was measured and results obtained as follows:-

Bridge	Box	Specific Conductance
8566	9000	1.066×10^{-6}
8656	9000	0.988 "
8787	9000	0.879 "
8366	9000	1.255 "

The capacity of the water cell used was 0.057307.

Conductivity of Acid.

Bridge	Box	Molar Conductance	Conc.
3556	70	80.7	0.01988
3551	70	80.8	"
3882	60	81.8	"
4346	50	81.03	"
4179	80	108.6	0.00993
4505	70	108.7	"
4884	60	108.8 ·	"
5345	50	108.1	"
4516	70	108.8	0.00988
4184	80	108.9	"
4884	60	109.3	"
4931	70	122.12	0.00745
4597	80	122.2	"
5910	60	143.5	0.00496
5533	70	143.6	"
6253	80	186.8	0.002481
6900	60	186.7	"
3551	70	81.1	0.0.0198
3910	60	81.2	"

The capacity of the cell used was 0.06196.

The above values were obtained as follows. Where L is the conductance of the solution, the specific conductance $\bar{L}$ was calculated by the formula, $\bar{L} = KL$, where K is the cell constant. From this, the molar conductance, Λ_c, was calculated

Alpha-Bromopropionic Acid
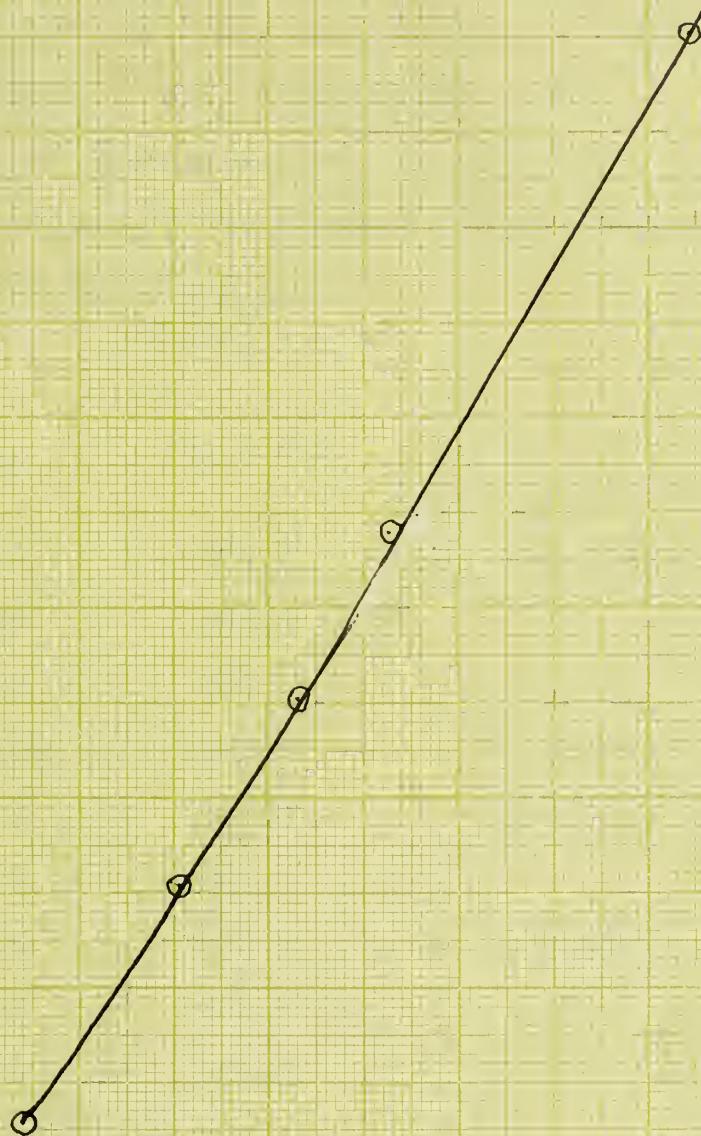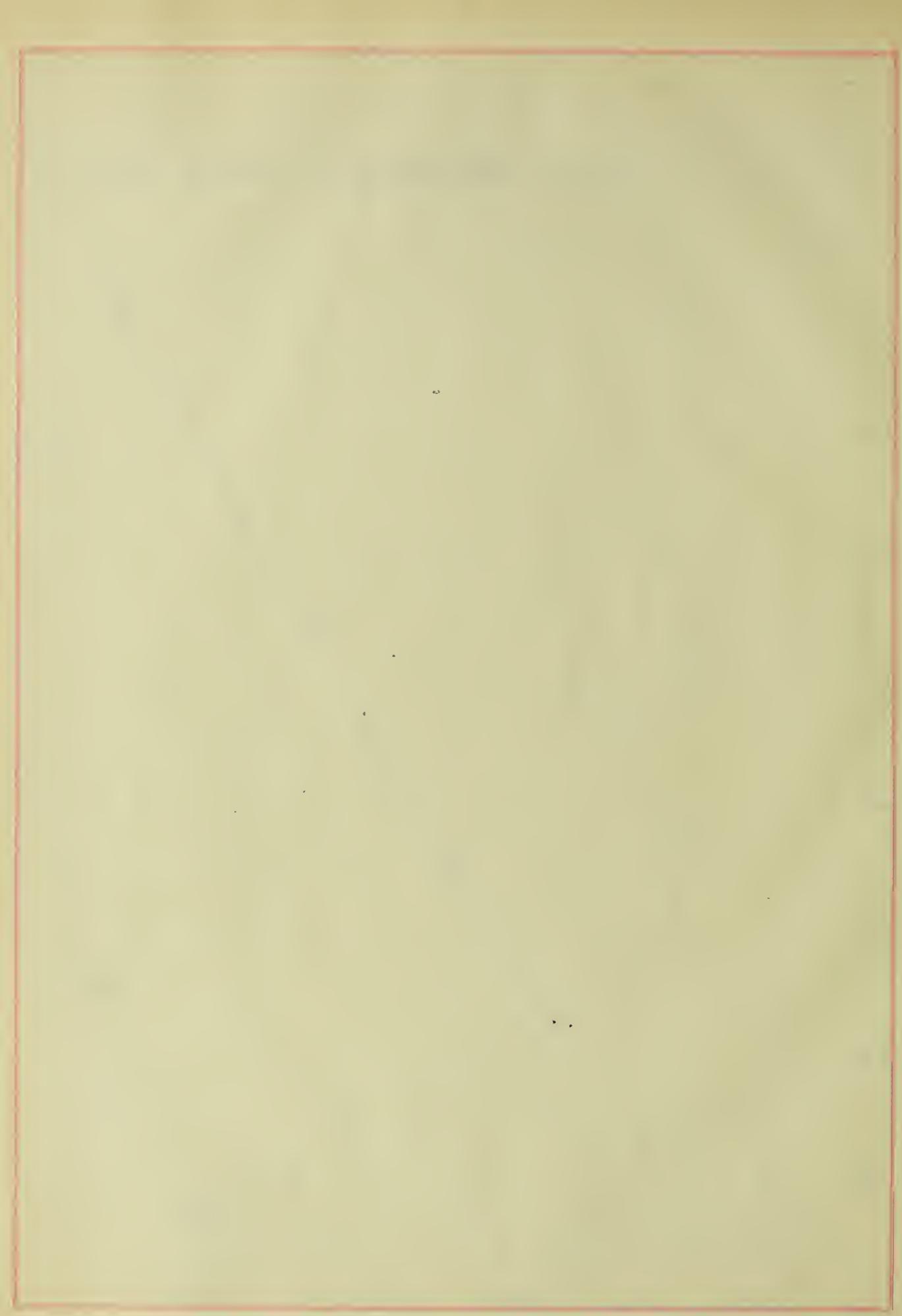
by means of $\Lambda = \dfrac{1000\,\overline{L}}{C}$, where C is the molal concentration of the solute per liter of solvent. A plot was then made of $(C\Lambda)^{n-1}$ against $\dfrac{1}{\Lambda}$. The value 2.00 for n was used, as this is the generally accepted value for weak electrolytes that obey the mass law. The Λ_0 value for the acid could not be obtained by exterpolation but was taken as 389 from the unpublished work of J.O. Carrero on beta-iodopropionic acid.

The Ionization Constant of Alpha-bromopropionic Acid.

The ionization constant of the alpha-bromoacid was calculated by the equation; $K = \dfrac{C(\Lambda)^2}{\Lambda_0(\Lambda_0^c - \Lambda_c)}$.

Concentration	Λ_c	$\Lambda_0 - \Lambda_c$	K (average)
0.01988	80.7	308.3	0.001082
"	80.8	308.2	
"	81.8	307.2	
"	81.03	307.97	0.001089
0.0198	81.1	307.9	0.001089
"	81.2	307.8	
0.00993	108.6	280.4	0.001076
"	108.7	280.3	
"	108.8	280.2	
"	108.6	280.4	
0.00988	108.8	280.2	0.001078
"	108.9	280.1	
0.00745	122.12	266.88	0.001078
"	122.2	266.84	
0.00496	143.5	245.5	0.001070

Concentration	Λ_c	$\Lambda_o - \Lambda_c$	K (average)
0.00496	143.6	245.6	
0.002481	186.8	202.2	0.001085

P. Walden, who measured the value of K in 1892, obtained the following results:

V	$C = \frac{1}{V}$	Λ	$\Lambda \times 1.063$ (Λ Corr.)		K (Corr.)	K (uncor.)
128	0.007812	110.4	117.3	269.	1.03×10^{-3}	1.08×10^{-3}
256	0.003906	145.1	154.3	232.	1.04 "	1.08 "
512	0.001953	185.3	197.0	189.	1.04 "	1.09 "
L024	0.0009766	225.0	239.2	147.	0.985 "	----

The corrected value, 1.04×10^{-3} , for K, as obtained by Walden is comparable to the average value here obtained, 1.072×10^{-3} . The difference between the two is 4.05 per cent.

In making his measurements given above, Walden used Siemen's units, which must be multiplied by 1.063 in order to convert his values for molar conductivity into modern international units. From the Λ_o value for sodium alpha-bromo-propionate was subtracted 51.2, the present accepted value for Λ_{oNa}. , and to this value for the molar conductivity of alpha-brompropionate ion at infinite dilution was added 347, the Λ_o value for Hydrogen ion in modern units, and the Λ_o for alpha-bromopropionic acid obtained. Walden's values for Λ_c at various concentrations were multiplied by the conversion factor and the values above obtained. Therefore the corrected values for Walden's K was obtainable from the following equation: $K_{Corr.} = \frac{c_c \Lambda^2_{(Corr.)}}{\Lambda_{o(Corr.)} (\Lambda_{o(Corr.)} \Lambda_{c(Corr.)})}$

CONCLUSIONS.

1.   The ionization constant of alpha-bromopropionic acid is found to be 1.08×10^{-3}, differing from Walden's value, 1.04×10^{-3}, by 4.05 per cent.

2.   The alpha-bromine influence in propionic acid is found to be 0.0206. Using Walden's value for $K_{\alpha Br}$ this constant is 0.0309.

BIBLIOGRAPHY.

(1) Ostwald : Z. f. phys. Ch., $\underline{3}$, 170, 241, 369.

(2) Derick : J. Am. Chem. Soc., $\underline{32}$, 999, (1910).

$\underline{33}$, 1167, 1181 (1911).

(3) Hollman : University of Ills. Thesis, 1912.

(4) Walden : Z. f. phys. Ch., $\underline{10}$, 650.

Stohmann and E. Franke : Z. f. phys. Ch., $\underline{16}$, 482.

Friedel and Machuca   : Ann. $\underline{120}$, 287.

Kekule′   : Ann. $\underline{130}$, 16.